

Nonequilibrium dynamics of polymer translocation: a mean-field model

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(Dated: February 2, 2008)

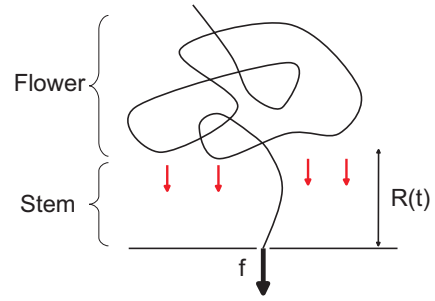
We analyse the dynamics of polymer translocation in the strong force regime by recasting the problem into solving a differential equation with a moving absorbing boundary. For the total translocation time, τ_{tr} , our simple mean-field model predicts that $\tau_{tr} \sim (\text{number of monomers})^{1.5}$, which is in agreement with the exponent found in previous simulation results. Our model also predicts intricate dependencies of τ_{tr} on the variations of the pulling force and of the temperature.

PACS numbers: 82.35.Lr, 83.50.-v, 87.15.He, 05.40.-a

I. INTRODUCTION

Understanding of polymer adsorption and translocation has important technological and biological significance. Besides well-known applications such as adhesion and coating, adsorption is responsible for facilitating breathing in the lungs [1] and translocation for the mechanism of transporting DNA and RNA across nuclear pores (e.g., see [2]). Although usually viewed as two different phenomena, adsorption and translocation are in fact very similar as both processes may be seen as having one end or both ends of a monomer chain pulled to an adsorbing surface. Indeed, simulation results have indicated that for a Rouse chain, both the total translocation time, τ_{tr} , and the total adsorption time τ_{ad} , scale like $M^{1.5}$ where M is the initial number of monomers in the polymer globule [3, 4]. Recently, it has also been recognised that many adsorption and translocation phenomena are in the strong force regime [2, 5], namely, bf is at least a few times of $k_B T$ where b is the bond length between connected monomers and f is the effective force exerted on the monomers in adsorption or in translocation. This suggests that polymer adsorption or translocation is likely to be a nonequilibrium process. Coupled with the well-known observations of ageing [6] and glassy behaviour [7, 8, 9] in adsorbed polymer layer, the need for a better understanding of the dynamics of polymer adsorption and translocation is in order. Here, we present a mean-field model that describes the dynamics of a polymer globule under translocation in the strong force regime. Letting the direction of the translocation process be in the negative z direction, we denote the number density of monomers in each xy -plane along the z axis by $\phi(t, z)$. The model is mean-field in the sense that the fluctuations in the x and y directions are averaged over. In the strong force regime, it is expected that the polymer will quickly adopt a “stem-flower” type configuration (c.f. Fig. 1) [10]. We thus set up a differential equation with the bottom of the “flower” as a moving absorbing boundary. The differential equation based model can be numerical solved very efficiently. As our model re-

FIG. 1: A schematic of the translocation process. The bottom-most monomers are cleared first and the resulting deviation in concentration from the equilibrium condition induces a pressure gradient that drives the monomers at the interface, a distance $R(t)$ away from the pore, to the bottom.



tains all spatial information along the z -axis, it provides better characterization of the translocation process. For instance, it allows for the determination of the temporal evolution of the centre of mass for the portion of the polymer to be translocated. Our model confirms the scaling law: $\tau_{tr} \sim M^{1.5}$, found in simulation results [4]. We also obtain novel quantitative predictions concerning how τ_{tr} would depend on the pulling force and thermal energy.

II. BACKGROUND

We are interested in the strong force regime, i.e., the effective force involved is more than a few times of $k_B T/b$ where b is the monomer-monomer bond length. In the case of adsorption, this translates to having the adsorption energy, ϵ , to be more than a few $k_B T$. In this regime, the polymer will be pulled strongly onto the surface and the time scale will generally be much quicker than the whole polymer relaxation time, $\tau_r = \frac{m\gamma M^2 b^2}{3\pi^2 k_B T}$ [11], where M is the number of monomers in the polymer, m is the mass of each individual monomer, γ is the monomer-solution collision frequency. The process is thus far from thermal equilibrium and local relaxation dominates. Our investigation is therefore fundamentally different from

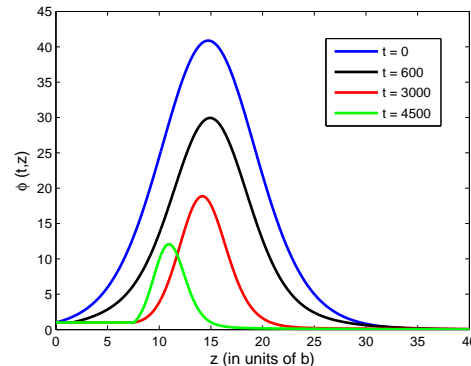
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much of the earlier works on polymer adsorption at equilibrium [11, 12, 13]. Nonequilibrium polymer adsorption dynamics has also recently received much attention and most studies focused on the scaling for the adsorption time, τ_{ad} , which for a Rouse chain is found to scale like $M^{1.5}$ [3, 14]. For further information on adsorption, we refer the readers to a recent review by O’Shaughnessy and Vavylonis [5]. In the case of polymer translocation, interest in the physics community is comparatively more recent and most early studies have focused on the low force regime, in which the relaxation time is shorter than the process of translocation. This allows for the use of the Fokker-Planck equation description [15, 16] or the nucleation theory [17, 18]. The validity of the above formalism has been questioned in [19] as it is argued that the relaxation time and translocation time are of the same order of magnitude. The authors further demonstrate the existence of anomalous dynamics in translocation through simulations and scaling argument. Anomalous dynamics in forced translocation was also studied in [20] and further explored in [21] with the use of fractional diffusion equation. More recently, the total translocation time for a Rouse chain, τ_{tr} , is investigated in [4] where the authors argue that the pulling force would only affect a small portion (a “fold”) of the polymer at a time and starting from this assumption, τ_{tr} is found by scaling argument to scale like $M^{1.5}$. However, Sakaue argued in [22] that the “folds” picture may only be correct when $bf/k_BT > M^{1/2}$. In the paper, the author treats the dynamics of translocation as a tension propagation problem and by assuming that each blob is at equilibrium locally, a differential equation governing the temporal evolution of M under translocation is formulated and then solved numerically. The approach is very similar in spirit to ours although there is one key difference: we treat the thermal diffusion and applied force separately while Sakaue group them together in the form of an effective force: $\tilde{f} = fR_0/k_BT$, where R_0 is the initial radius of the polymer globule. In terms of predictions, for a Rouse chain in the strong pulling regime, our model and Sakaue’s model both give $\tau_{\text{tr}} \sim M^{1.5}$, in agreement with simulation results [4]. On the other hand, our model indicates a much more complex relationship for τ_{tr} ’s dependencies on f and k_BT . In particular, we find that the scaling law: $\tau_{\text{tr}} \sim f^{-1}$ is only true when $f/k_BT \rightarrow \infty$, and that τ_{tr} is found to depend non-monotonically on the thermal energy.

III. A DISCUSSION ON SCALING

For the problem at hand, the dimensionful parameters are: f, k_BT, b, γ and m , with M as the only dimensionless parameter. If we let the total translocation time, τ_{tr} , be given by the function: $\phi(f, k_BT, b, \gamma, m, M)$. We can invoke the intuitive Π -theorem [23] to transform the

FIG. 2: Temporal evolution of $\phi(t, z)$ with $m\gamma = 1$, $b = 1$, $f = 10$, $D = 1$ and $M = 500$. The times are in units of τ_0 . Notice the gradual lengthening of the stem attached to the pore at $z = 0$.



functional dependency into the following form:

$$\tau_{\text{tr}} = \tau_0 \Phi \left(\frac{bf}{k_BT}, \frac{k_BT}{mb^2\gamma^2}, b, \gamma, m, M \right) \quad (1)$$

where $\tau_0 = \frac{m\gamma b}{3\pi^2 k_BT}$ is the single monomer diffusion time [11], and Φ is now dimensionless and as such, it can only depend on the first two and the last parameters, i.e.,

$$\tau_{\text{ad}} = \tau_0 \Phi \left(\frac{bf}{k_BT}, \frac{k_BT}{mb^2\gamma^2}, M \right), \quad (2)$$

The above equation is exact except for, of course, the fact that we do not know what Φ is.

In [4], the author’s ansatz for the form of Φ is:

$$\Phi \left(\frac{bf}{k_BT}, \frac{k_BT}{mb^2\gamma^2}, N \right) = \text{const.} \times \frac{k_BT}{bf} N^{3/2}. \quad (3)$$

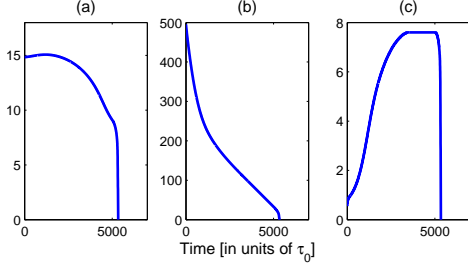
Namely, it is assumed that the second argument in Φ is redundant. There is no physical reasoning for this particular ansatz. Indeed, we find in this paper that all three arguments affect Φ independently even in the range $10 \leq bf/k_BT \leq 500$, which is not described in [4, 22].

IV. A MEAN-FIELD MODEL

Before we move on to describing our model, we remark that in this paper, we ignore all interactions from monomers that have passed through the pore. Namely, we assume that the pulling force is strong enough that the chain on the other side of the pore does not have any effect on the chain being translocated. The same assumption is made in [4, 22] and it renders our analysis more similar to the phenomenon of adsorption and so the findings here may be relevant to both phenomena.

The basic observation concerning translocation is that as the first monomer of a polymer globule is being

FIG. 3: Some properties of $\phi(t, z)$ with parameters as defined in the caption of Fig. 2. (a) Center of mass for the portion of polymer awaiting translocation (in units of b). (b) Number of monomers, $M(t)$. (c) The length of stem (in unit of b).



dragged through the pore (c.f. Fig. 1), the monomer number density at the bottom of the coil gradually decreases. This imbalance in monomer concentration from the equilibrium condition will induce an osmotic pressure that pushes the globule towards the surface. As a result, it accelerates the adsorption process. Starting with this observation, we let $\phi(t, z)$ be the expected number of monomers at time t and position z . In other words, $\phi(t, z)$ has dimension length^{-1} . Denoting the total number of monomers by M and the center of mass by \bar{z} , we write $\hat{\phi}_{M, \bar{z}}$ as the monomers distribution at equilibrium. Given any other distribution, ϕ , we assume that the osmotic pressure to be proportional to the difference between the current distribution and the distribution at equilibrium: $\phi - \hat{\phi}_{M, \bar{z}}$ (c.f. Ch. VII in [11]). In other words, if we ignore adsorption for the time being, the temporal equation on the distribution is:

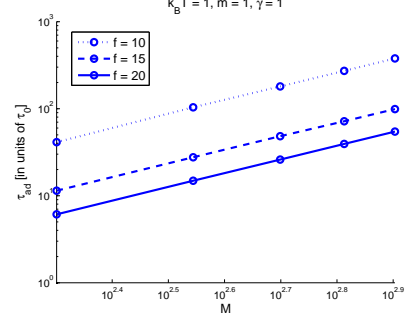
$$\frac{\partial \phi}{\partial t} = D \nabla^2 (\phi - \hat{\phi}_{M, \bar{z}}) \quad (4)$$

where D is the diffusion constant and is assumed to be $k_B T / m \gamma$. We note that as a deterministic model, the above equation does not model diffusion of the whole molecules, i.e., \bar{z} does not vary and as such, the model is meant to present the dynamical behaviour at short time in comparison to the whole globule relaxation time, $\tau_r = M^2 \tau_0$. This assumption is consistent with the parameter set we study here as τ_{tr} is always less than 10 percents of τ_r .

We now incorporate translocation into the model. If the monomers are not connected, the adsorption process may be modelled as a fixed absorbing boundary in the diffusion equation. But since the monomers are connected and as such the pulling force can propagate through the chain, the differential equation above becomes a moving boundary problem and we have the following model equation:

$$\frac{\partial \phi}{\partial t} = \begin{cases} -\frac{f}{m \gamma b R} & , \text{ for } z = R(t) \\ D \nabla^2 (\phi - \hat{\phi}_{M, \bar{z}}) & , \text{ for } z > R(t). \end{cases} \quad (5)$$

FIG. 4: Adsorption times with respect M . It is found that $\tau_{ad} \sim M^{1.5}$.



where $R(t) = \max[z : \phi(t, z) < b \text{ and } 0 \leq z \leq \bar{z}(t)]$, and f is the pulling force. We also maintain that $\phi(z, t) = 1$, for $0 \leq z < R(t)$, which represents the stem connecting the pore and the flower (c.f. Fig. 1). In the above equation, $R(t)$ is the moving absorbing boundary with a constant absorbing rate $-\frac{f}{m \gamma b R}$. The rate equation can be obtained from the force-velocity equation:

$$-\frac{bf}{m \gamma R} = v = b^2 \frac{\partial \phi}{\partial t}. \quad (6)$$

By dimensional analysis, we know that $\hat{\phi}_{M, \bar{z}}(z) \equiv \hat{\phi}_{M', \bar{z}}((M'/M)^\nu z)$ where ν is $3/5$ for a chain in good solvent and it is $1/2$ for a chain in θ solvent [11]. In other words, if we know $\hat{\phi}_{M(0), 0}$, we can obtain all the other distributions $\hat{\phi}_{M, \bar{z}}$ by simple translation and dilation.

In summary, we have constructed a differential equation model that depends purely on a set of constant parameters: $f, m, b, \gamma, k_B T$, and a static distribution $\hat{\phi}_{M(0), 0}$ that can be determined once and for all. Eq. 5 is the main result of this paper and it can be numerically solved efficiently (c.f. Appendices A and B for simulation details). We will now focus on the various predictions made by our model on the Rouse chain.

V. RESULTS AND DISCUSSION

Since the pulling force is strong, the diffusion process is not rapid enough to replenish the supply of monomer near the pore and so a stem forms naturally as shown in Fig. 2. This renders an initial increase in separation between the center of mass and the pore as the bottom monomers are quickly translocated (c.f. Fig. 3 (a)). To understand the scaling law: $\tau_{tr} \sim M^{1.5}$ (c.f. Fig. 4), one can imagine the scenario where $k_B T \rightarrow 0$. In this situation, the globule is completely frozen throughout the translocation process. Now, since the initial size of the polymer globule is $\sim b \sqrt{M_0}$ where M_0 denotes the initial number of monomers, the stem will be of the same order

of magnitude in length for most of the translocation process. Therefore, as a first approximation, one can set up the following differential equation as in Eq. 6:

$$-\frac{f}{m\gamma b\sqrt{M_0}} = \frac{\partial M(t)}{\partial t}, \quad (7)$$

and the scaling law will then follow immediately. In other words, the scaling is purely due to the fact that the monomers being dragged to the pore are on average a distance of $\sim b\sqrt{M_0}$ away. This is a much simpler explanation of the scaling law than that presented in [4] and it highlights that the “fold” picture may not be necessary in explaining the scaling behaviour seen in single chain translocation [24].

If the pulling force is increased, it is natural to expect that τ_{tr} will decrease. This is indeed the case, but deviation from the expected scaling law: $\tau_{tr} \sim f^{-1}$ can be seen even for the range $10 \leq bf/k_B T \leq 500$ (c.f. Fig. 5). This is different from the expectation described in [4, 22]. In fact, our results suggests that the above scaling only holds at the limit $f/k_B T \rightarrow \infty$ and as such, highlight the important role of the thermal energy.

If the temperature is increased, the diffusion process (indicated by the red arrows in Fig. 1) induced by the osmotic pressure is facilitated and one would expect an decrease in τ_{tr} . Although this is generally the case, it is surprising to see the opposite trend at the low-temperature-high-force regime (c.f. Fig 6). This counter intuitive feature may be understood by the fact that at low temperature, as the force is becomes large, the center of mass of the remaining polymer is driven away from the pore quickly (as shown in Fig. 3) and this *escape* process is aided by a slight increase in diffusion as the temperature is increased.

In conclusion, we have formulated a simple mean-field model for polymer translocation that captures the effect of local diffusion. Our model is capable of confirming the scaling law: $\tau_{tr} \sim M^{1.5}$, as observed in simulations [4], and predicts an intricate τ_{tr} ’s dependencies on the pulling force and the thermal energy. Our work thus signals an interesting new territory that awaits exploration.

Acknowledgments

The author thanks the Glasstone Trust (Oxford) and Jesus College (Oxford) for financial support.

APPENDIX A: FITTING FOR $\hat{\phi}_{M,\bar{z}}$

For a Rouse chain in three dimensions with $b = 1$, we find that the following function is a good approximation for $\hat{\phi}$:

$$\hat{\phi}_{M,\bar{z}}(z) = \frac{\sqrt{M}}{2} \exp \left[P \left(\frac{z - \bar{z}}{\sqrt{M}} \right) \right] \quad (A1)$$

FIG. 5: Adorption time vs. pulling force. The results indicate that the scaling law: $\tau_{tr} \sim f^{-1}$ is only true asymptotically as $k_B T \rightarrow 0$, and deviation from it can be observed even for $k_B T = 0.04$ and for the range $10 \leq f \leq 500$.

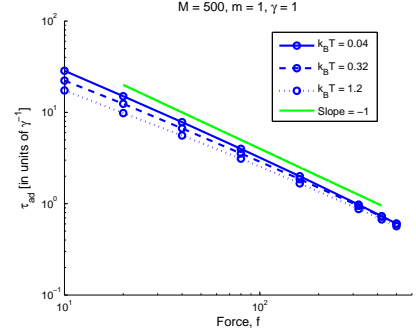
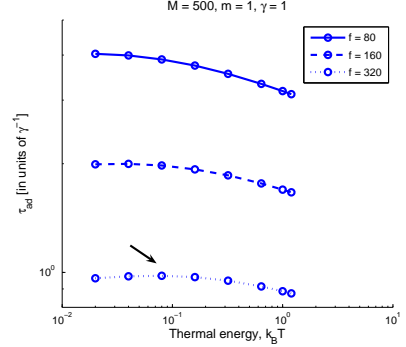


FIG. 6: Adorption time vs. thermal energy. Notice that as f increases, τ_{tr} can become non-monotonic with respect to $k_B T$ as shown by the peak indicated by the black arrow.



where $P(x)$ is

$$-0.6x^{10} + 4x^8 - 9.48x^6 + 11.21x^4 - 11.94x^2 + 1.27 \quad (A2)$$

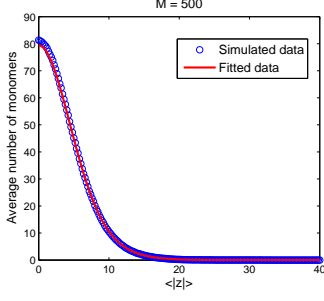
for $|x| < 1.44$ and $\hat{\phi}_{M,0}(x) = 0$ otherwise (c.f. Fig. 7). This functional form is used in our numerical integration although this approximation step by an closed form function is not necessary. Instead, one can formulate a lookup table for $\nabla^2 \hat{\phi}_{M,\bar{z}}$ from sampling.

APPENDIX B: DETAILS ON SIMULATION METHOD

In solving the differential equation Eq. 5, we employ the finite element method. Namely, we denote $\phi(t_n, z_j)$ by ϕ_j^n where t_n and z_j are the grid points on time and on position. In our simulations, $\Delta t = 0.001\gamma^{-1}$ and $\Delta z = 0.05b$. Specifically, our algorithm is as follows:

1. Given M and a time grid and a position grid with spacing Δt and Δz , set $n = 0$, $\bar{z} = 0$, and for all j ,

FIG. 7: Fitting by the expression shown in Eq. A1.



set $\phi_j^0 = \hat{\phi}_{M,0}(z_j)$ where $\hat{\phi}_{M,0}$ is given in Appendix A. Let $p_0 = \max[j : \phi_j^0 < 1 \text{ and } z_j < \bar{z}]$, set $s = z_{p_0}$, $R = \Delta z$ and $v = \frac{bf}{mR\gamma}$.

2. For $j > p$, set ϕ_j^{n+1} as

$$\phi_j^n + D\Delta t \left(\frac{\phi_{j+1}^n - 2\phi_j^n + \phi_{j-1}^n}{\Delta z^2} - \nabla^2 \hat{\phi}_{M,\bar{z}} \right) - \Delta t v \delta_{j,p+1}.$$

3. For $p_0 \leq j \leq p$, set ϕ_j^{n+1} to 1.

4. Set M as $M - v\Delta t$ and $\bar{z} = \sum_j z_j \phi_j^{n+1} / \sum_j \phi_j^{n+1}$. Renormalise $\sum_j \phi_j^{n+1}$ to M by re-scaling ϕ_j^{n+1} .

5. Let $p = \max[j : \phi_j^{n+1} < 1 \text{ and } z_j < \bar{z}]$, set $R = z_p - s + \Delta z$ and $v = \frac{bf}{mR\gamma}$.

6. If $M < 1$, stop; otherwise, increment n by 1 and go back to 2.

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